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TIME-TEMPERATURE STUDIES OF HIGH TEMPERATURE DETERIORATION PHEN--ETC(U)

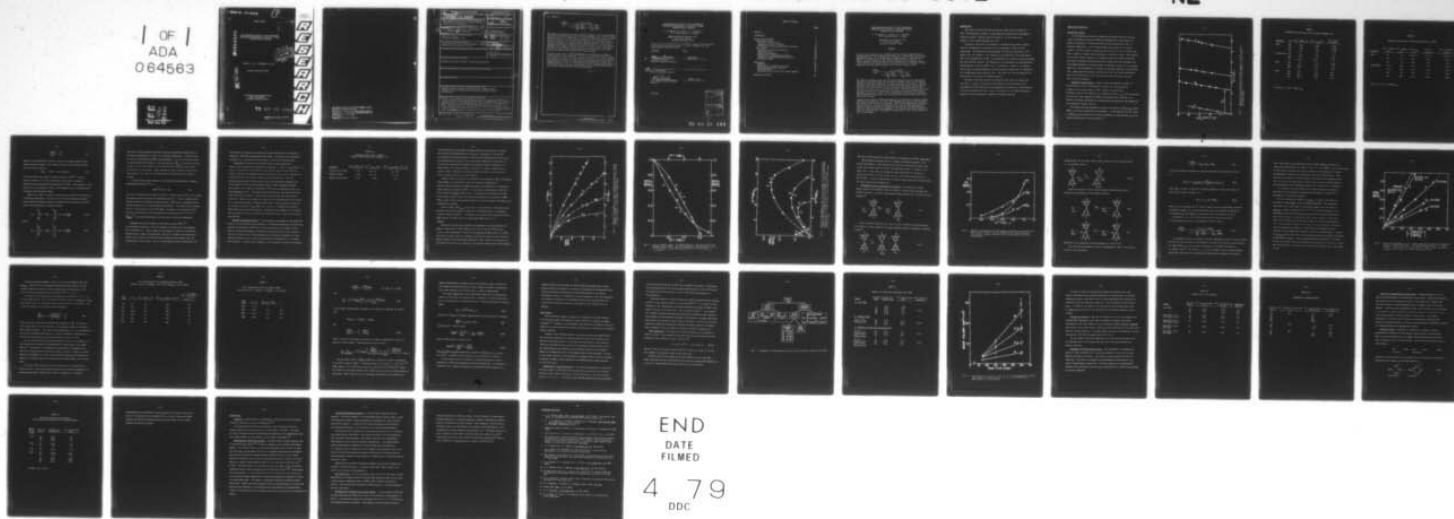
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DETERIORATION PHENOMENON IN LUBRICANT SYSTEMS:
SYNTHETIC ESTER LUBRICANT

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20. ABSTRACT

$$-\frac{d(\text{BPH})}{dt} = \frac{w_o + 2k_1 (\text{ROOH})_t}{2 + 2 \frac{k_{\text{QM}}}{k_{\text{BPH}}} \frac{(\text{QM})_t}{(\text{BPH})_t} + 2 \frac{k_{\text{P}}}{k_{\text{BPH}}} \frac{(\text{P})_t}{(\text{BPH})_t}}$$

The symbol w_o designates the rate of radical formation from the spontaneous reaction of molecular oxygen with PETH and $2k_1(\text{ROOH})_t$ is the rate of radical production from the decomposition of organic hydroperoxides formed at high BPH concentrations from the reactions of BPH and BPH antioxidant active products, QM and P, with organic peroxy radicals and at low BPH concentrations from reactions of organic peroxy radicals with PETH. The ratios $k_{\text{QM}}/k_{\text{BPH}}$ and $k_{\text{P}}/k_{\text{BPH}}$ are the ratios of rate constants for the free radical hydrogen atom transfer reactions of QM and P to that of BPH. The general validity of this equation and the values of the various rate constants will now be obtained from stirred flow reactor studies.

A study of wear rates at 100°C manifested by pure PETH and by slightly oxidized PETH has been completed. At only ca. 2% oxidation the wear rate is increased by a factor of 8 over that of pure PETH. This result together with those from various ancillary studies are consistent with the view that hydroperoxides, perhaps in combination with α, γ -substituted difunctional oxidation products, lead to a rapid corrosive wear phenomena. The separate and combined effects of model hydroperoxide and α, γ -dicarbonyl compounds on the wear of pure PETH will now be investigated.

alpha, gamma

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SYNTHETIC ESTER LUBRICANT

L. R. Mahoney, S. Korcek, P. A. Willermet,
E. J. Hamilton and R. K. Jensen

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Report to the Air Force Office of Scientific Research of work carried
out during the time period October 1, 1977 to September 30, 1978
under contract F44620-76-C-0097.

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ABSTRACT

A study of the lengths of the inhibition periods caused by the addition of varying amounts of the bisphenol antioxidant, 4,4'-methylenebis (2,6-di-tert-butylphenol), BPH, on the autoxidation of pentaerythrityl tetraheptanoate, PETH, in a batch reactor at 180, 200 and 220°C has been carried out. A kinetic analysis based upon these results together with preliminary results on the BPH decay and quinone methide product formation as a function of time yield the following general equation for the rate of decay of BPH,

$$-\frac{d(\text{BPH})_t}{dt} = \frac{w_o + 2k_1(\text{ROOH})_t}{2 + 2\frac{k_{\text{QM}}}{k_{\text{BPH}}} \frac{(\text{QM})_t}{(\text{BPH})_t} + 2\frac{k_{\text{P}}}{k_{\text{BPH}}} \frac{(\text{P})_t}{(\text{BPH})_t}}$$

The symbol w_o designates the rate of radical formation from the spontaneous reaction of molecular oxygen with PETH and $2k_1(\text{ROOH})_t$ is the rate of radical production from the decomposition of organic hydroperoxides formed at high BPH concentrations from the reactions of BPH and BPH antioxidant active products, QM and P, with organic peroxy radicals and at low BPH concentrations from reactions of organic peroxy radicals with PETH. The ratios $k_{\text{QM}}/k_{\text{BPH}}$ and $k_{\text{P}}/k_{\text{BPH}}$ are the ratios of rate constants for the free radical hydrogen atom transfer reactions of QM and P to that of BPH. The general validity of this equation and the values of the various rate constants will now be obtained from stirred flow reactor studies.

A study of wear rates at 100°C manifested by pure PETH and by slightly oxidized PETH has been completed. At only ca. 2% oxidation the wear rate is increased by a factor of 8 over that of pure PETH. This result together with those from various ancillary studies are consistent with the view that hydroperoxides, perhaps in combination with α, γ -substituted difunctional oxidation products, lead to a rapid corrosive wear phenomena. The separate and combined effects of model hydroperoxide and α, γ -dicarbonyl compounds on the wear of pure PETH will now be investigated.

INTRODUCTION

This report describes the work carried out under contract F44620-76-C-0097, "Time-Temperature Studies of High Temperature Deterioration Phenomena in Lubricant Systems: Synthetic Ester Lubricants", for the period from October 1, 1977 through September 30, 1978.

During this time period the formation of disubstituted, primary products from the autoxidation of pentaerythrityl tetraheptanoate, PETH, has been established. This important finding together with the work described in the annual report of October 1, 1977 resulted in the completion of the experimental work on the autoxidation of PETH. The preparation of a technical paper describing the work entitled, "Kinetics and Mechanism of the Autoxidation of Pentaerythrityl Tetraheptanoate at 180 and 200°C" by E. J. Hamilton, S. Korcek, L. R. Mahoney, and M. Zinbo is nearing completion and after internal review will be forwarded to the funding agency under separate cover. This paper will then be submitted for publication to the Journal of Organic Chemistry.

The bulk of the work carried out during the time period is divided into two areas: a study of the kinetics and mechanism of the reactions in the autoxidation of PETH inhibited by the bisphenolic antioxidant 4,4'-methylene-bis(2,6-di-tert-butylphenol) and a study of the effects of the PETH autoxidation products on the wear behavior of PETH as a boundary lubricant.

RESULTS AND DISCUSSION

Antioxidant Studies

In the following sections are summarized the results obtained from the study of inhibited oxidation of PETH and n-hexadecane in the presence of a phenolic antioxidant 4,4'-methylenebis(2,6-di-tert-butylphenol), BPH, at elevated temperatures. All of these studies were carried out in a batch reactor. The batch reactor requires the use of only 35 to 40 ml of PETH from which a number of samples may be obtained as a function of time. This compares to the 100 or more ml required for a single stirred flow reactor experiment. The results obtained from these batch reactor experiments have provided, with the minimum consumption of purified PETH, considerable insight into the kinetic behavior of the antioxidant as a function of reaction temperature and concentration. Based upon these results a series of stirred flow reactor experiments will now be carried out to test and refine the model developed from the batch reactor experiments.

Inhibition Period Studies - Figure 1 shows the inhibitory effects of varying amounts of BPH on hydroperoxide formation in the autoxidation of PETH with molecular oxygen at 180°C. Results obtained from a systematic study of the lengths of the inhibition periods, t_{inh} , the time periods for which the chain oxidation of PETH and n-hexadecane are suppressed, as a function of initial antioxidant and hydroperoxide concentrations and temperature are presented in Tables I and II.

The results are best discussed in terms of the values of $(BPH)_0/t_{inh}$, where $(BPH)_0$ is initial concentration of antioxidant. In the simplest case the values of $(BPH)_0/t_{inh}$ are related to the rates of formation of free radicals, R_1 , in an oxidizing hydrocarbon by the expression, ⁽¹⁾

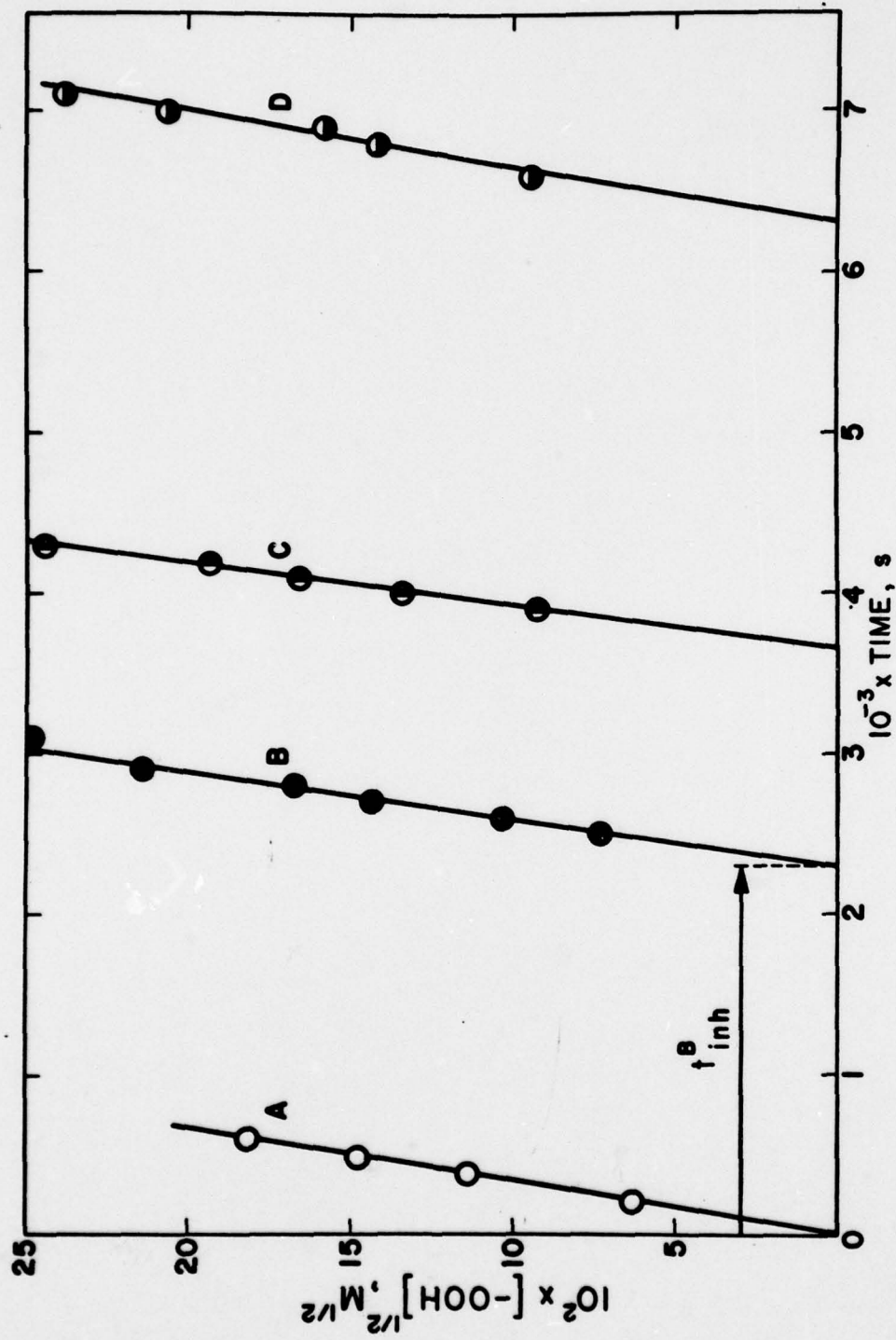


Fig. 1 - Inhibition period measurement for PETH oxidation at 180°C. Initial BPH concentrations: A - 0, B - $1.09 \times 10^{-4}M$, C - $1.86 \times 10^{-4}M$, D - $3.45 \times 10^{-4}M$.

TABLE I

Inhibition Period Study of Pure Systems $((\text{ROOH})_0 \approx 0)$

Substrate	T °C	$10^4 \times (\text{BPH})_0 \text{ (M)}$	$10^{-3} \times t_{\text{inh}} \text{ (sec)}$	$10^7 \times R_i/n^a$ (M-sec ⁻¹)
PETH	180	1.09	2.28	0.478
	180	1.86	3.66	0.508
	180	3.45	6.28	0.549
n-hexadecane	180	2.12	1.91	1.11
	180	7.96	7.36	1.08
	180	48.8	22.5	2.17
PETH	200	5.3	1.33	3.98
	200	10.6	2.74	3.87
	200	15.7	3.48	4.51
PETH	220	39.1	1.24	31.5
	220	50.6	1.28	39.5
	220	76.2	1.64	46.5

^a From eq. I $R_i/n = (\text{BPH})_0/t_{\text{inh}}$

TABLE II

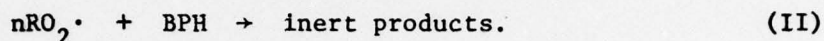
Inhibition Period Study in Preoxidized Systems at 180°C

Substrate	$10^4 \times (\text{ROOH})_0$ (M)	$10^4 \times (\text{BPH})_0$ (M)	$10^{-3} \times t_{\text{inh}}$ (sec)	R_i/n^a (M-sec ⁻¹)	$10^4 \times R_i/n(\text{ROOH})$ (sec ⁻¹)
PETH	60	7.2	(1.0-1.4)	(5.1-7.2)	(0.85-1.2)
	114	17.5	1.62	10.8	0.95
	144	7.0	0.39	17.9	1.24
n-hexadecane	55.2	19.5	3.25	6.0	1.09
	60.1	13.0	1.89	6.9	1.14
	129	22.0	1.66	13.3	1.03
	273	38.1	1.55	24.6	0.90

^a From eq. I $R_i/n = (\text{BPH})_0/t_{\text{inh}}$

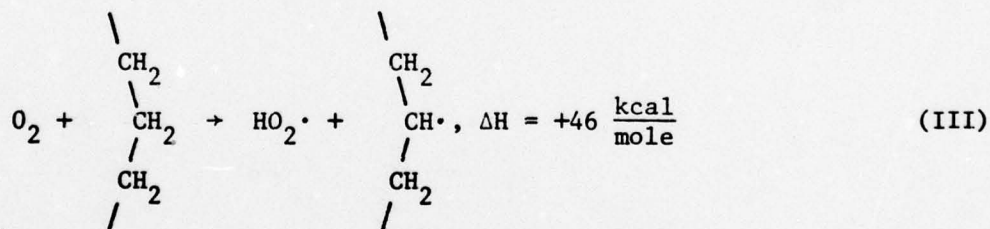
$$\frac{(\text{BPH})_0}{t_{\text{inh}}} = \frac{R_i}{n} \quad (\text{I})$$

where \underline{n} , the stoichiometric factor, is equal to the total number of free radical species consumed in the complete reaction of one molecule of BPH and its reactive products,

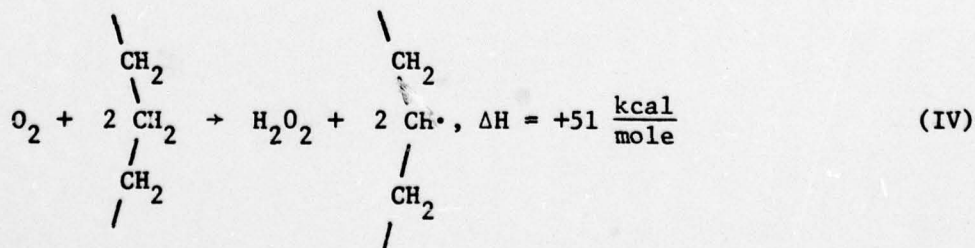


At 60° and 120°C the \underline{n} values for BPH are equal to 4.0.^(2a,b) From the results in Table I we see that the values of R_i/n show a systematic increase with increasing initial concentration of BPH. The magnitude of this effect was very pronounced at 220°C. This suggests that R_i increases and/or \underline{n} decreases with increasing $(\text{BPH})_0$.

There are at least two types of reactions which produce free radicals in an oxidizing hydrocarbon. The first, the so called spontaneous reactions, involve highly endothermic hydrogen atom abstraction reactions from the C-H bonds of the hydrocarbon by molecular oxygen,

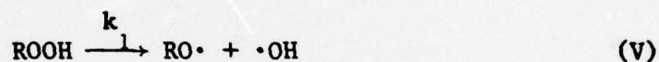


and/or



The rates of the spontaneous reactions should be approximately proportional to the molar concentrations of $-\text{CH}_2-$ in an oxidizable hydrocarbon. The molar ratio of $-\text{CH}_2-$ in n-hexadecane and PETH are approximately 2 as are the relative values or R_i/n from the data in Table I. Also the value of $\Delta E_{(R_i/n)}^\ddagger$ calculated from the values of R_i/n at low $(\text{BPH})_0$ from the 180° and 200°C experiments was found to be equal to ca. 48 kcal/mole. These findings are thus consistent with the view that reactions III and IV are important in the formation of free radical species.

A second source of free radicals is the homolytic decomposition of organic hydroperoxide products,⁽³⁾ i.e.,



Even at low concentrations of ROOH the rates of radical production from this process can greatly exceed those from the spontaneous reactions. Table II summarizes the results obtained from inhibition period studies in PETH and in n-hexadecane which had been preoxidized to form ROOH before BPH addition. The values of R_i/n increase 10 fold in the presence of $60 \times 10^{-4}\text{M}$ ROOH. Furthermore, the magnitude of this increase is proportional to the hydroperoxide concentration and the values of $\frac{R_i}{n(\text{ROOH})}$ ⁽⁴⁾ are within experimental error the same in PETH and n-hexadecane.

Although there may be changes in the value of \underline{n} with $(\text{BPH})_0$,⁽⁵⁾ our preliminary conclusion is that the changes in the ratio R_i/n are primarily due to changes in R_i . These changes in pure systems are caused by the thermal decomposition of organic hydroperoxides, reaction V, formed by the reactions of organic peroxy radicals with BPH and BPH antioxidant active products when the concentration of BPH is high. When the concentration of BPH is sufficiently low

and BPH does not suppress the reactions of peroxy radicals with the substrate completely, additional hydroperoxides are formed. This leads to an exponential increase in R_i . Such overview finds support in the result reported below.

Independent of mechanism, the above results and those reported in Table III have considerable technological significance. Values of $t_{inh}/(BPH)_0$, i.e., $1/(R_i/n)$, calculated from the results of the present study with pure PETH are likely to represent the maximum inhibition periods per molar unit of BPH that can be realized in the service use of PETH at a given temperature. Since the maximum concentrations of BPH utilized in the fully formulated lubricants are in the range of $10^{-2}M$ one would calculate that if PETH containing $10^{-2}M$ BPH were exposed to an oxidative environment at $220^{\circ}C$ rapid autoxidation would occur within one hour or less. The present calculation does not take into account the effects of partial pressure of oxygen which would increase the time period of protection. However, such effects are likely to be counterbalanced by the effects due to impurities present in technical grade PETH. From the results in Table III we see that the values of $t_{inh}/(BPH)_0$ are a factor of 6 smaller with technical grade PETH than the purified materials. Percolation over alumina of the technical grade material results in a material with inhibition times 4 times lower than the pure material.

Reactant and Product Analysis - At this stage of development of the analytical method, we have encountered some difficulty in obtaining reproducible values for the absolute concentrations of BPH and its reaction products as a function of time. When the liquid chromatographic instrument is dedicated solely to the analyses of a series of samples from a single experiment and a series of standards are simultaneously analyzed, values of absolute concentration reproducible to ± 3 percent may be obtained. However, due to demands by other laboratory projects the analyses

TABLE III

Inhibition Period Study at 180°C;
Effect of PETH Purification ($(\text{ROOH})_0 \approx 0$)

<u>Substrate</u>	<u>$10^4 \times (\text{BPH})_0 \text{ (M)}$</u>	<u>$10^{-3} \times t_{\text{inh}} \text{ (sec)}$</u>	<u>$10^{-6} \times t_{\text{inh}} / (\text{BPH})_0 \text{ (M}^{-1} \text{ sec)}$</u>
Technical Grade PETH	3.50	ca. 1.0	ca. 2.9
Percolated PETH	3.60	ca. 1.8	ca. 5.0
Highly Purified PETH	3.45	6.28	18

are interrupted, the instrument settings and modes of operation are changed, and extensive restandardization is necessary to reproduce (to better than ± 10 percent) the absolute values of concentration obtained at an earlier time. The reproducibility problem is less severe when comparisons of the ratios of the relative concentrations derived from integrated signal intensities, i.e., $(\text{BPH})_t/(\text{BPH})_0$ and $(\text{Product})_t/(\text{BPH})_t$, are made on a series of samples over a period of time. Therefore, the present results are given in the ratio form and are reproducible to ± 5 percent absolute.

Figure 2 shows the values of the ratios of the integrated signal intensities, $(\text{BPH})_t/(\text{BPH})_0$, as a function of time for a series of experiments in which varying concentrations of BPH were added to pure PETH and to n-hexadecane before exposure to oxygen at 180°C . At low initial concentrations of BPH the decay curves are convex; curves B and C. As the initial concentration of BPH is increased, curves D and E, the convexity decreases and the slopes of $(\text{BPH})_t/(\text{BPH})_0$ versus time are approximately constant for each run within the range of the concentrations studied.

Plots of $(\text{BPH})_t/(\text{BPH})_{0(18)}$ versus time for pure PETH and a PETH system which had been reacted with oxygen to produce $60 \times 10^{-4}\text{M}$ ROOH prior to the addition of BPH are shown in Figure 3. In contrast to the decay curves observed with pure PETH, curve D, the decay curve for preoxidized PETH, curve F, is concave.

Concurrent with the decay of BPH is the formation of quinone methide, QM. Figure 4 shows plots of $(\text{QM})_t/(\text{BPH})_0$ versus time for the pure PETH (curves C and D), pure n-hexadecane (curve E), and preoxidized PETH (curve F) at 180°C . The nature of these curves is consistent with the view that the QM is an intermediate product of the antioxidant reactions of BPH. Further, the dependence of the maximum yield of QM as a function of the initial concentration of BPH suggests

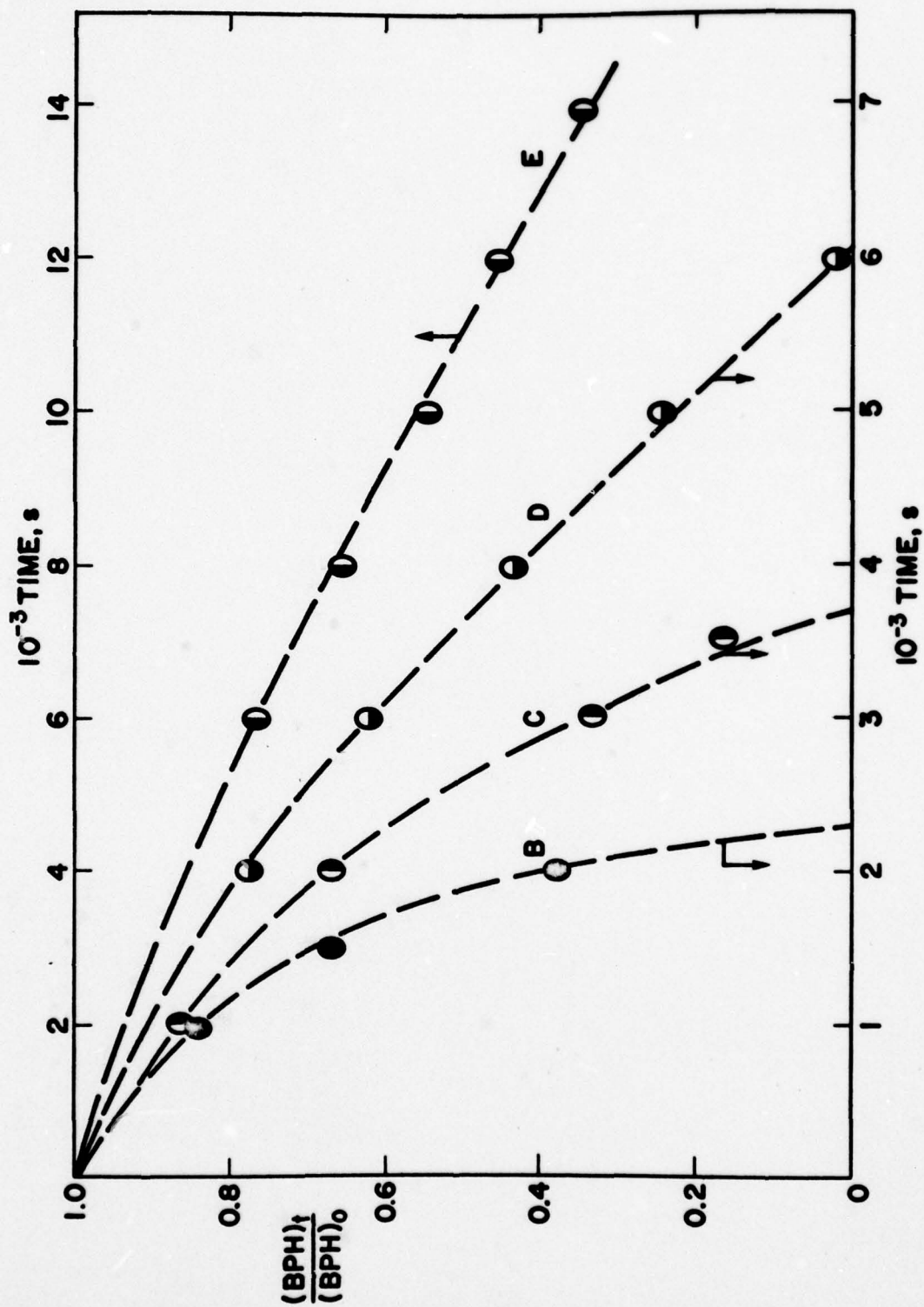


Fig. 2 - Ratios of $(BPH)_t / (BPH)_o$ vs. time for PETH and n-hexadecane (curve E) oxidations at $180^\circ C$. Initial BPH concentrations: B - $1.09 \times 10^{-4} M$, C - $1.86 \times 10^{-4} M$, D - $3.45 \times 10^{-4} M$, E - $48.8 \times 10^{-4} M$.

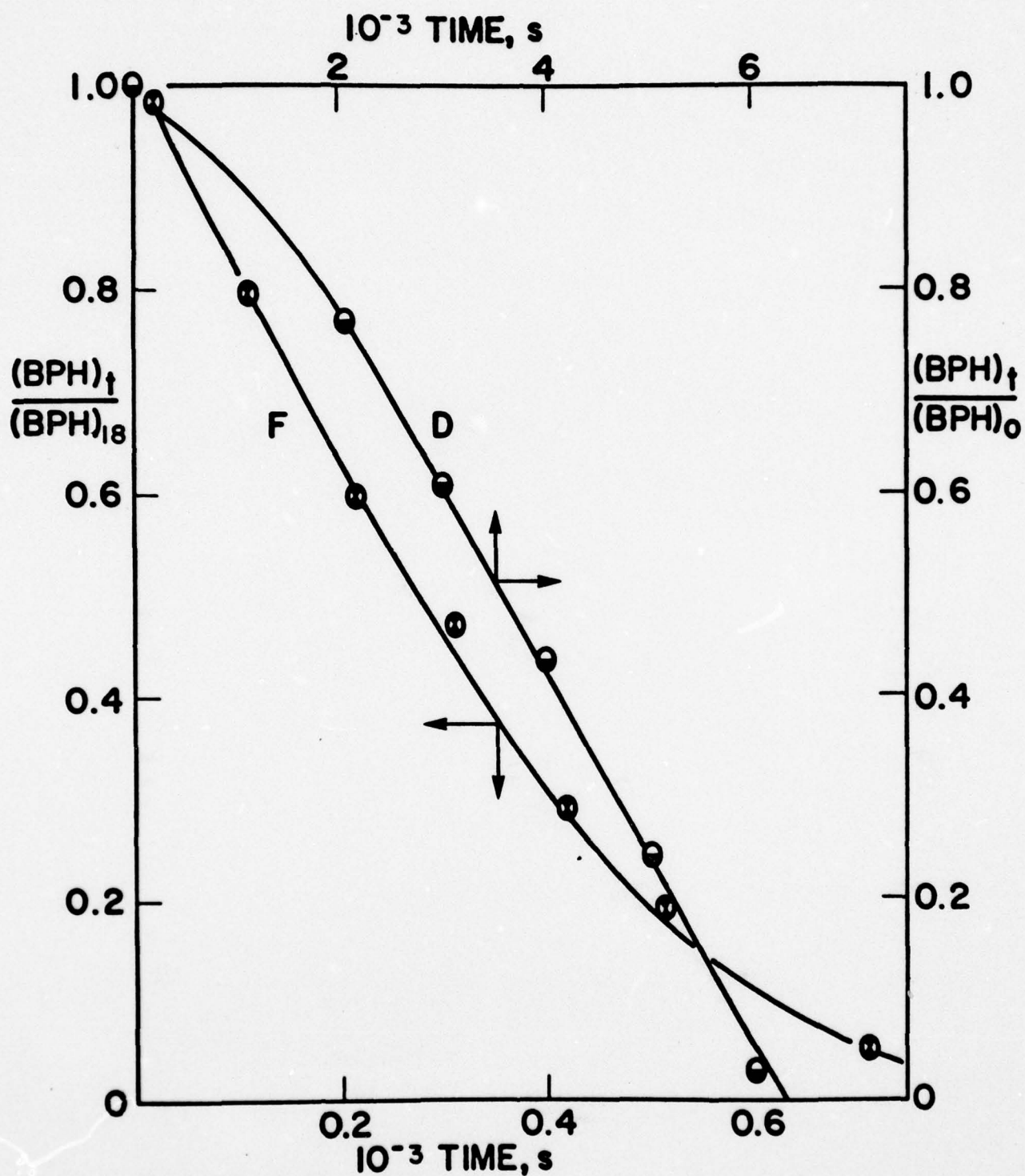


Fig. 3 - Ratios of $(BPH)_t/(BPH)_0$ and $(BPH)_t/(BPH)_{18}$ vs. time for pure and pre-oxidized PETH at 180°C. Initial hydroperoxide concentrations: D - 0, F - $60 \times 10^{-4}M$. Initial BPH concentrations: D - $3.45 \times 10^{-4}M$, F - $7.2 \times 10^{-4}M$.

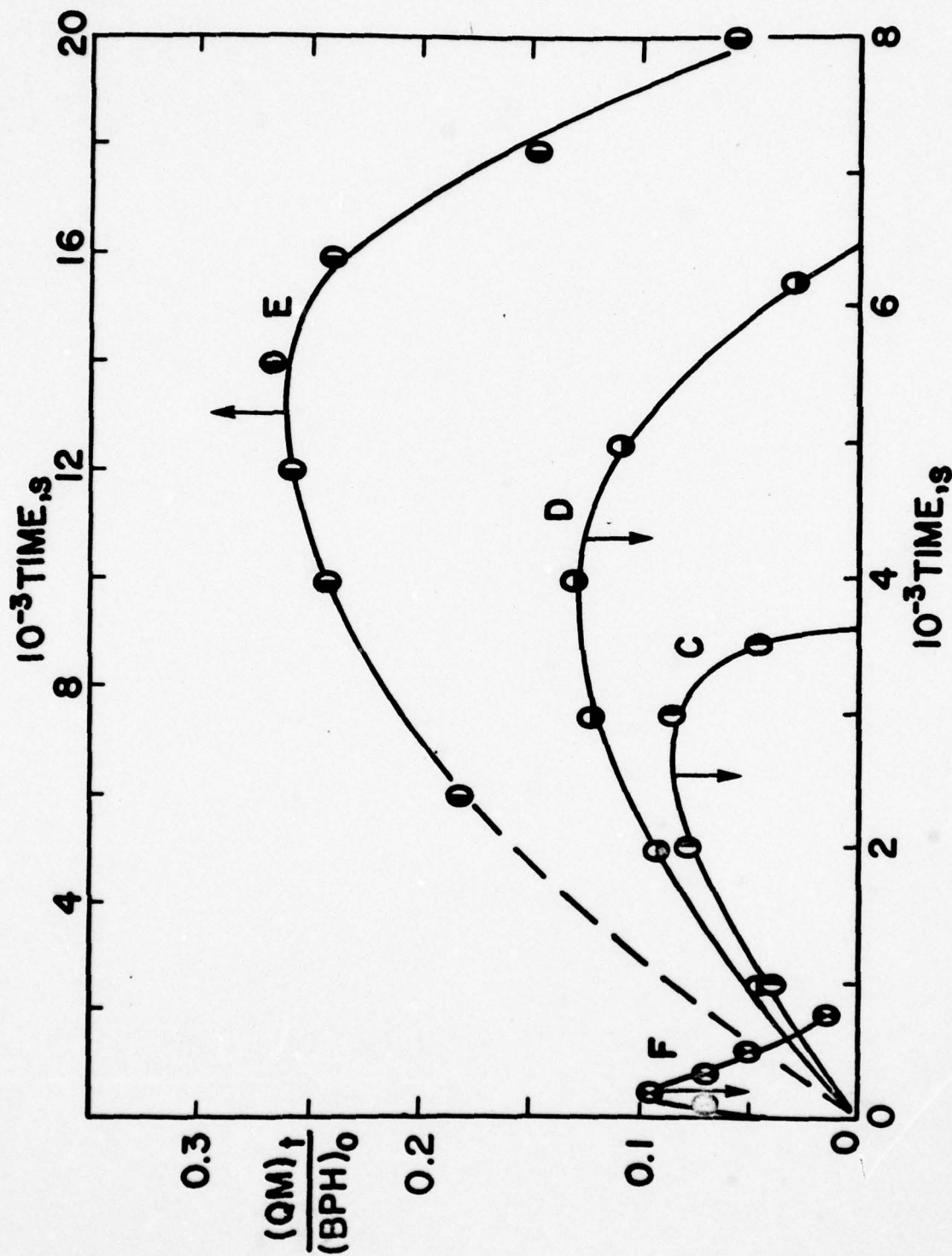
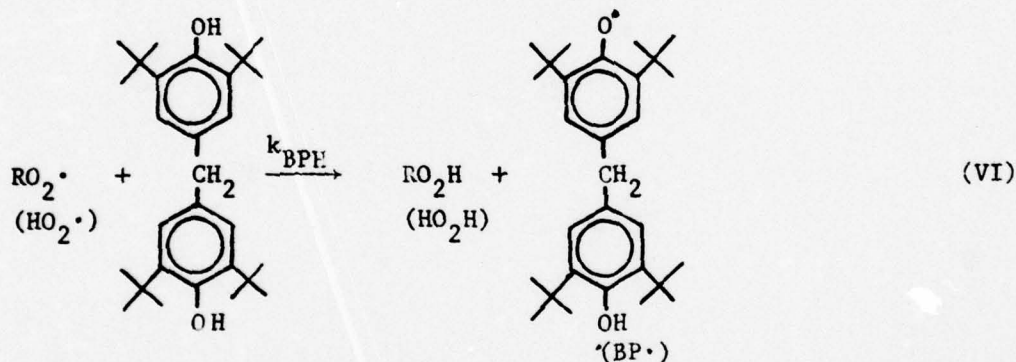


Fig. 4 - Ratios of $(QM)_t / (BPH)_0$ vs. time for pure (curves C and D) and preoxidized (curve F) PETH and n-hexadecane (curve E) at 180°C . Initial hydroperoxide concentrations: C, D, and E - 0, F - $60 \times 10^{-4}\text{M}$. Initial BPH concentrations: C - $1.86 \times 10^{-4}\text{M}$, D - $3.45 \times 10^{-4}\text{M}$, E - $48.8 \times 10^{-4}\text{M}$, F - $7.2 \times 10^{-4}\text{M}$.

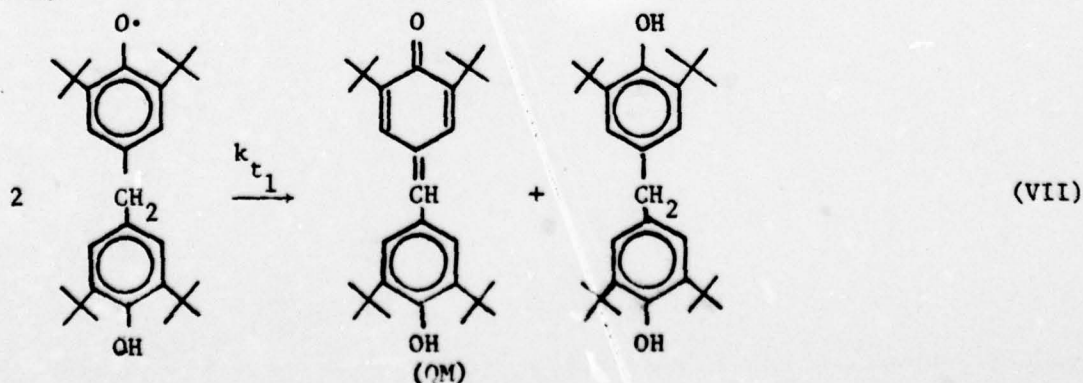
that QM is being consumed by radical species in competition with BPH, vide infra.

Besides BPH and QM peaks there is a number of unidentified peaks in the liquid chromatograms. Some peaks grow and then decay with reaction time, while others first appear toward the end of the inhibition period. In Figure 5 are shown plots of the ratios of integrated signal intensities for QM and two unidentified products to BPH_t versus time for a pure PETH system inhibited by BPH at 200°C. In future work we hope to identify these species and develop methods for their quantitative determination.

Preliminary Kinetic and Mechanistic Analyses - The reactions of peroxy radical species with bisphenol, BPH, are likely to involve facile hydrogen atom transfer reactions to form the corresponding phenoxy radical, BP^\bullet , and hydroperoxide products, (1)



A pair of phenoxy radicals, BP^\bullet , then undergoes a bimolecular disproportionation reaction to form a molecule of quinone methide, QM, and to regenerate a molecule of BPH, (6)



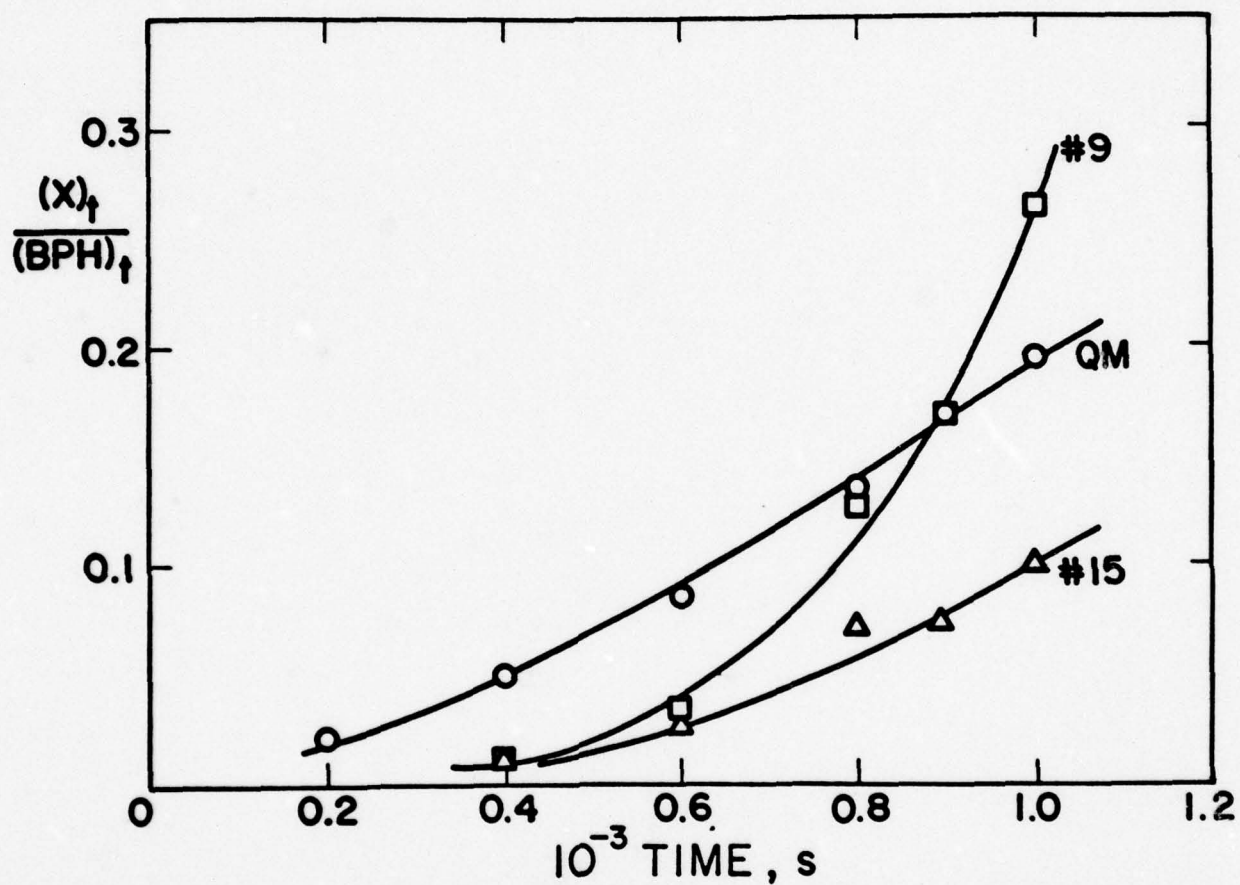
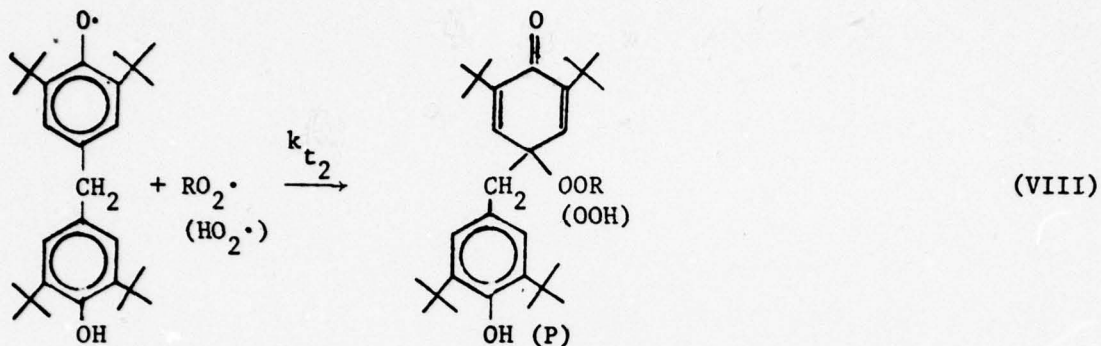
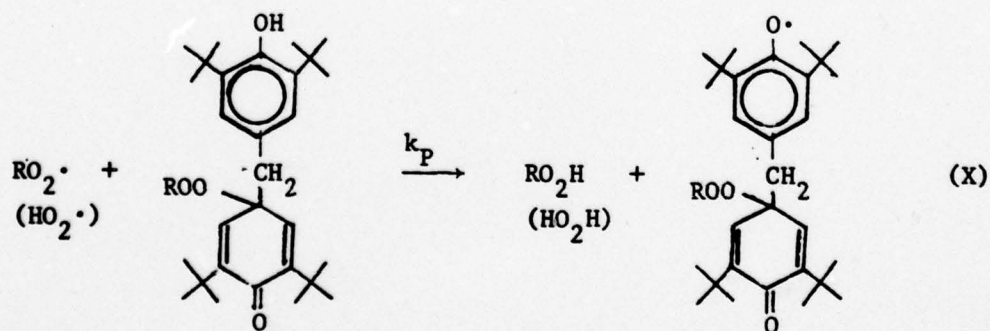
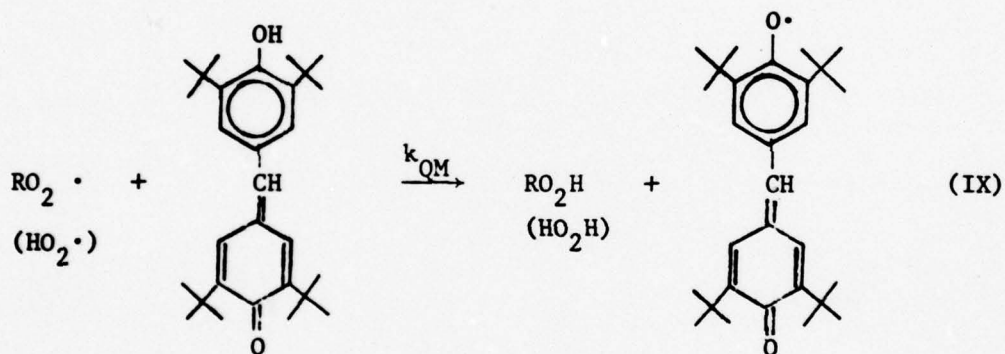


Fig. 5 - Ratios of concentrations of BPH oxidation products to concentration of BPH vs. time at 200°C. Initial concentration of BPH was equal to 5.3×10^{-4} M. Products #9 and #15 refer to peak numbers in liquid chromatograph.

Alternatively, $BP\cdot$ can react with a peroxy radical to form a second product, P, in reactions such as,



Since both QM and P contain reactive phenolic groups they may also function as antioxidants by the transfer reactions,



followed by fast termination reactions analogous to those of $BP\cdot$.

From this reaction sequence the rate of consumption of BPH at any time, t , is given by the expression,

$$-\frac{d(\text{BPH})_t}{dt} = k_{\text{BPH}} (\text{RO}_2)_t (\text{BPH})_t \quad (\text{XI})$$

If all free radicals terminate by reactions with BPH and its products, QM and P,

$$(\text{RO}_2)_t = \frac{(R_i)_t}{2 k_{\text{BPH}} (\text{BPH})_t + 2 k_{\text{QM}} (\text{QM})_t + 2 k_{\text{P}} (\text{P})_t} \quad (\text{XII})$$

where $(R_i)_t$ is equal to the rate of radical formation at time t and consist of the sum of at least two terms, i.e.,

$$(R_i)_t = w_o + 2k_1 (\text{ROOH})_t, \quad (\text{XIII})$$

where w_o is the constant rate of radical formation from the spontaneous reactions of molecular oxygen, k_1 is the pseudo first order rate constant for homolysis of hydroperoxide, and $(\text{ROOH})_t$ is the hydroperoxide concentration at time t .

Combining eqs. XI, XII and XIII then yields the general expression for the instantaneous rate of disappearance of BPH at time t ,

$$\frac{-d(\text{BPH})_t}{dt} = \frac{w_o + 2 k_1 (\text{ROOH})_t}{2 + 2 \frac{k_{\text{QM}}}{k_{\text{BPH}}} \frac{(\text{QM})_t}{(\text{BPH})_t} + 2 \frac{k_{\text{P}}}{k_{\text{BPH}}} \frac{(\text{P})_t}{(\text{BPH})_t}} \quad (\text{XIV})$$

By appropriate choice of values for the rate constants and ratios of rate constants, equation XIV could account for the changes in the nature of the decay curves observed for $(\text{BPH})_t / (\text{BPH})_{o(18)}$ in the presence or absence of preformed hydroperoxide, cf. Figures 2 and 3. When $(\text{ROOH})_t \gg w_o / 2k_1$ the numerator does not change significantly while the value of the denominator monotonically increases with reaction

time. This leads to the exponential decay of $(\text{BPH})_t/(\text{BPH})_{18}$ observed with preformed hydroperoxides (cf. Figure 3, curve F). When $(\text{ROOH})_t \leq w_o/2 k_1$ the values of the numerator increase with reaction time due to the homolysis of organic hydroperoxides formed via the antioxidant reactions of BPH, QM, and P. This increase can compensate for the increase in the value of the denominator and lead to the observed approximately constant rate of decay of $(\text{BPH})_t/(\text{BPH})_o$ in the pure PETH and pure n-hexadecane systems (cf. curves D and E in Figure 2).

It is possible with the present data to make preliminary estimates of the ratios of rate constants in equation XIV and provide a test for the plausibility of the kinetic analysis.

We first consider the values of $k_{\text{QM}}/k_{\text{BPH}}$. In Figure 6 are plots of the values of $(\text{QM})_t/(\text{BPH})_t$ versus $\{1 - [(\text{BPH})_t/(\text{BPH})_o]^{1/2}\}$. The linearity of these plots over a wide range of conversions suggests that the value of $k_{\text{QM}}/k_{\text{BPH}}$ is equal to approximately 1.5.^(7,8) If the sole product of the antioxidant reactions of BPH was QM, the slope of such plots would be 2.0. The observed slopes at low $(\text{BPH})_o$ are only a small fraction of that value while with the highest concentration of $(\text{BPH})_o$ the slope is approximately 1.8. The systematic increase in the values of these slopes with increasing initial concentration of BPH are in the direction anticipated from the occurrence of the competitive reactions to form P as outlined above. A value of $k_{\text{QM}}/k_{\text{BPH}}$ greater than unity is in line with results derived from calorimetric and equilibrium studies of the corresponding phenoxy radicals.⁽⁹⁾ In those studies it was shown that the bond energy of the phenolic O-H in QM is 3.6 kcal/mole lower than that of the O-H in the 2,4,6-tri-tert-butylphenol, a good model for BPH.

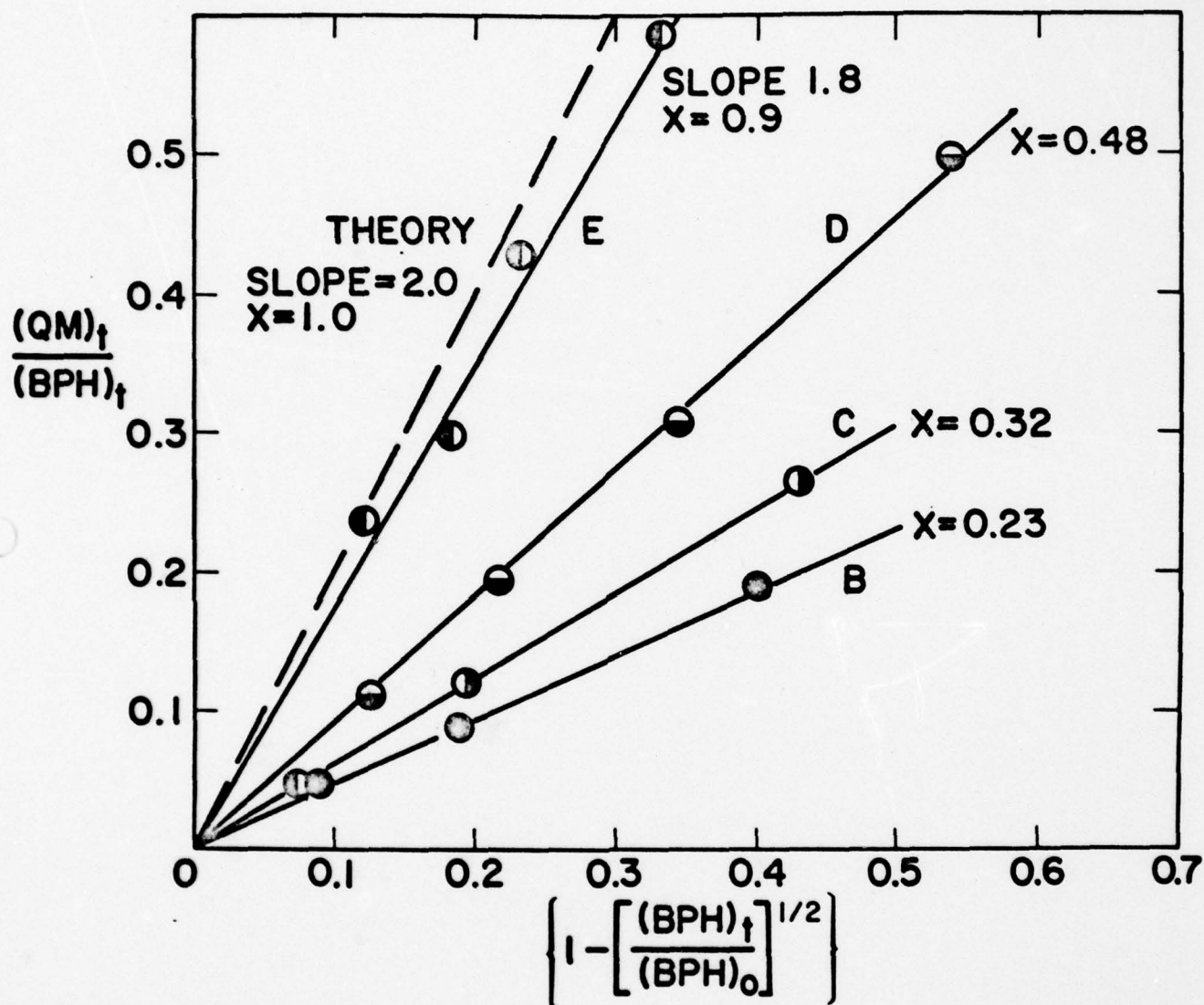


Fig. 6 - Ratios of $(QM)_t/(BPH)_t$ vs. $\left\{1 - \left[\frac{(BPH)_t}{(BPH)_0}\right]^{1/2}\right\}$ for PETH and n-hexadecane (curve E) oxidations at 180°C. Initial BPH concentrations: B - $1.09 \times 10^{-4}M$, C - $1.86 \times 10^{-4}M$, D - $3.45 \times 10^{-4}M$, E - $48.8 \times 10^{-4}M$. The values \underline{x} equal to the yields of QM from the reactions of BPH.

From the following argument a value of 0.5 may be assigned to the ratio k_P/k_{BPH} . Since there is no extended conjugation in either BPH or in P the relative molecular reactivity of these species will be proportional to the ratio of their abstractable phenolic hydrogens,⁽¹⁰⁾ i.e., 2 to 1.

The values of the denominator in equation XIV, designated $(2 + \Sigma)_t$, for a given experiment may then be calculated from these values of k_{QM}/k_{BPH} , k_P/k_{BPH} , the observed values of $(QM)_t/(BPH)_t$ and calculated values of $(P)_t/(BPH)_t$. The values $(P)_t/(BPH)_t$ were calculated from the equation,

$$\frac{(P)_t}{(BPH)_t} = 2 (1-x) \left\{ \left(\frac{(BPH)_0}{(BPH)_t} \right)^{\frac{1}{2}} - 1 \right\} \quad (XV)$$

where x is equal to the yield of QM from the reactions of BPH. The value of x for a given run is equal to the ratio of the observed slopes to the theoretical slope in Figure 4. The values of the denominator, $(2 + \Sigma)_t$, calculated for one run with preoxidized PETH and one run with pure PETH are summarized as a function of reaction times in the second column of Tables IV and V.

For the system with preformed hydroperoxides the value of $2k_1(ROOH)_t$ may be calculated from the values of the hydroperoxide concentration of the samples and k_1 .⁽⁴⁾ The ratios of the numerator in equation XIV to denominator as a function of time are given in the final column of Table IV. Since w_0 is small compared to $2k_1(ROOH)_t$, cf. below, the values of the ratios of the numerator to denominator correctly predict the concave decay of $(BPH)_t/(BPH)_0$ with reaction time.

In the pure PETH system the initial concentration of hydroperoxide is essentially zero. Since the observed rates of decay of BPH are independent of conversion from 2000 to 5000 sec (cf. curve D of Figure 2), it follows:

TABLE IV

Fit of Equation XIV for Preoxidized PETH at 180°C
(Curve F in Fig. 3; $(\text{ROOH})_0 = 62 \times 10^{-4} \text{M}$; $(\text{BPH})_{18} \approx 6.8 \times 10^{-4} \text{M}$)

Time (sec)	$(2 + \Sigma)_t$	$10^4 \times (\text{ROOH})_t \text{ (M)}$	$10^8 \times 2k_1 (\text{ROOH})_t \text{ (M-sec}^{-1}\text{)}$	$10^8 \times \frac{2k_1 (\text{ROOH})_t}{(2 + \Sigma)_t^2} \text{ (M-sec}^{-1}\text{)}$
18	2.0	62	248	124
109	2.35	58	233	99
211	2.68	62	248	92
310	2.78	58	232	83
413	3.22	62	247	77
510	3.76	66	264	70

TABLE V

Fit of Equation XIV for Pure PETH at 180°C
 (Curve D in Fig. 3; $(\text{ROOH})_0 \approx 0$; $(\text{BPH})_0 = 3.9 \times 10^{-4} \text{ M}$)

Time (sec)	$(2 + \Sigma)_t$	$\left(\frac{1}{\alpha}\right)_w / 2k_1 (\text{BPH})_0$	α
2000	2.44	-	-
3000	2.88	0.6	0.8
4000	3.32	0.7	0.9
5000	4.60	0.4	0.5

$$\frac{-d(\text{BPH})_t}{dt} = \frac{-d(\text{BPH})_{2000}}{dt} \quad \text{for } 2000 \leq t \leq 5000$$

and

$$\frac{w_o}{2k_1} = \frac{(2 + \Sigma)_{2000} (\text{ROOH})_t - (2 + \Sigma)_t (\text{ROOH})_{2000}}{(2 + \Sigma)_t - (2 + \Sigma)_{2000}} \quad (\text{XVI})$$

If the organic hydroperoxide is formed by the reactions of BPH and its products then

$$(\text{ROOH})_t \approx \alpha \left[(\text{BPH})_o - (\text{BPH})_t \right],$$

and

$$\frac{(\text{ROOH})_t}{(\text{BPH})_o} \approx \alpha \left[1 - \frac{(\text{BPH})_t}{(\text{BPH})_o} \right] \quad (\text{XVII})$$

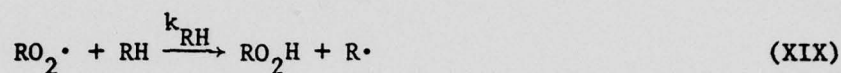
where α is equal to the number of molecules of organic hydroperoxide formed per molecule of BPH consumed. Combining equations XVI and XVII,

$$\left(\frac{1}{\alpha} \right) \frac{w_o}{2k_1 (\text{BPH})_o} = \frac{(2 + \Sigma)_{2000} \left[1 - \frac{(\text{BPH})_t}{(\text{BPH})_o} \right] - (2 + \Sigma)_t \left[1 - \frac{(\text{BPH})_{2000}}{(\text{BPH})_o} \right]}{(2 + \Sigma)_t - (2 + \Sigma)_{2000}} \quad (\text{XVIII})$$

The calculated values of $\left(\frac{1}{\alpha} \right) \frac{w_o}{2k_1 (\text{BPH})_o}$ as a function of time are summarized in the third column of Table V. Utilizing values of $2k_1$ equal to $4 \times 10^{-4} \text{ sec}^{-1}$,⁽⁴⁾ $(\text{BPH})_o$ equal to $3.9 \times 10^{-4} \text{ M}$ and a value of w_o equal to $20 \times 10^{-8} \text{ M/sec}$ ⁽¹¹⁾ values of α equal to 0.8 at 3000 seconds, 0.90 at 4000 seconds, and 0.50 at 5000 seconds are calculated. These values of α are in the range anticipated for the formation of

organic hydroperoxides from BPH and its active products since a fraction of the hydrogen atom abstractions are by $\text{HO}_2\cdot$ radicals and ROOH is undergoing a first order homolytic decay process with $t_{1/2}$ equal to 3500 seconds.

The highly convex decay curves exhibited by BPH when its concentration decays to a low level, see curves B and C in Figure 2, can then be accounted for by the occurrence of an additional mode of organic hydroperoxide formation, namely



The rate of formation of organic hydroperoxides from this process is given by

$$\frac{d\text{ROOH}}{dt} = k_{\text{RH}} (\text{RO}_2\cdot) (\text{RH}). \quad (\text{XX})$$

Combining eqs XX and XI yields

$$\frac{d(\text{ROOH})}{dt} = \frac{k_{\text{RH}}(\text{RH})}{k_{\text{BPH}}} \left[- \frac{1}{(\text{BPH})} \frac{d(\text{BPH})}{dt} \right]. \quad (\text{XXI})$$

Thus for ROOH formed by reaction XIX

$$(\text{ROOH})_t^{\text{XIX}} = \frac{k_{\text{RH}}(\text{RH})}{k_{\text{BPH}}} \ln \frac{(\text{BPH})_0}{(\text{BPH})_t}. \quad (\text{XXII})$$

When $k_{\text{BPH}}(\text{BPH}) \leq k_{\text{RH}}(\text{RH})$ exponential increases in $(\text{ROOH})_t$ and in R_i occur and lead to the observed strong convexity of curves B and C in Figure 2.

At this point we are in a position to initiate stirred flow reactor experiments on PETH and n-hexadecane systems containing BPH. The validity of equation XIV for a general description of the BPH inhibited systems can be

readily tested since the volume of reacted material generated from a single experiment may be sufficient to determine the hydroperoxide concentrations and allow the isolation by preparative liquid chromatography of the various intermediate products. In addition, it will be possible to carry out experiments with admixture of BPH and its intermediate products and thus determine with considerable precision the values of the ratios of rate constants such as k_{QM}/k_{BPH} .

Wear Studies

There have been a number of studies of the effects of the wear behavior of lubricants caused by the addition of small amounts of a variety of organic compounds.⁽¹²⁾ However, to our knowledge, there have been no studies of the wear behavior of a well characterized synthetic lubricant as a function of its degree of thermal oxidation.

As noted in our original proposal, the stirred flow reactor method allows the convenient preparation of autoxidized PETH in quantities sufficient for a variety of such wear studies. At the same time application of the analytical techniques developed during the course of the thermal oxidation studies allows the characterization and analysis of the oxidation products in the original samples and changes that occur in the samples after a wear experiment. As part of the current contract we have initiated a systematic study of the wear behavior of samples of highly purified PETH and of autoxidized PETH obtained from the stirred flow reactor.

Composition of Starting Materials - The initial experiments were carried out utilizing samples of PETH which had been purified by percolation over alumina, followed by high vacuum distillation and then followed by a second percolation treatment over alumina. A portion of this purified material was then autoxidized

in the stirred flow reactor at 180°C for a residence time equal to 360 seconds. The hydroperoxide titer of the autoxidized PETH was equal to 420×10^{-4} M while the organic acid titer was equal to 160×10^{-4} M, both being measured at room temperature.

From these analytical values and from the results obtained from the detailed analyses of very similar samples of autoxidized PETH⁽¹³⁾ it is possible to make estimates of the concentrations of various autoxidation products of PETH in the sample utilized for the wear study. This is shown in Figure 7. The estimates for a number of species were made from the results obtained by direct quantitative analyses or from quantitative analyses of the products of LiAlH_4 reductions. These species are enclosed in solid lines in the figure. Species for which only qualitative analytical results were obtained and which account for the unique kinetic behavior of the autoxidation of PETH are enclosed in dashed lines.

Wear Experiments - The results of the wear experiments are summarized in Table VI A and B. Wear volumes for the lower 3 balls were calculated from the average wear scar diameter by Feng's equation,⁽¹⁴⁾

$$V = 4.65 \times 10^{-2} d^4 - 3.21 \times 10^{-5} Wd \quad (\text{XXIII})$$

where \underline{V} is equal to the wear volume in mm^3 for 3 balls, \underline{d} is equal to the wear scar diameter in mm and \underline{W} is equal to the load in kg.

From the plots of wear volume versus time, Figure 8, we see that under these conditions the wear rates observed when using the oxidized PETH samples are a factor of 8 times higher than those observed with purified PETH.

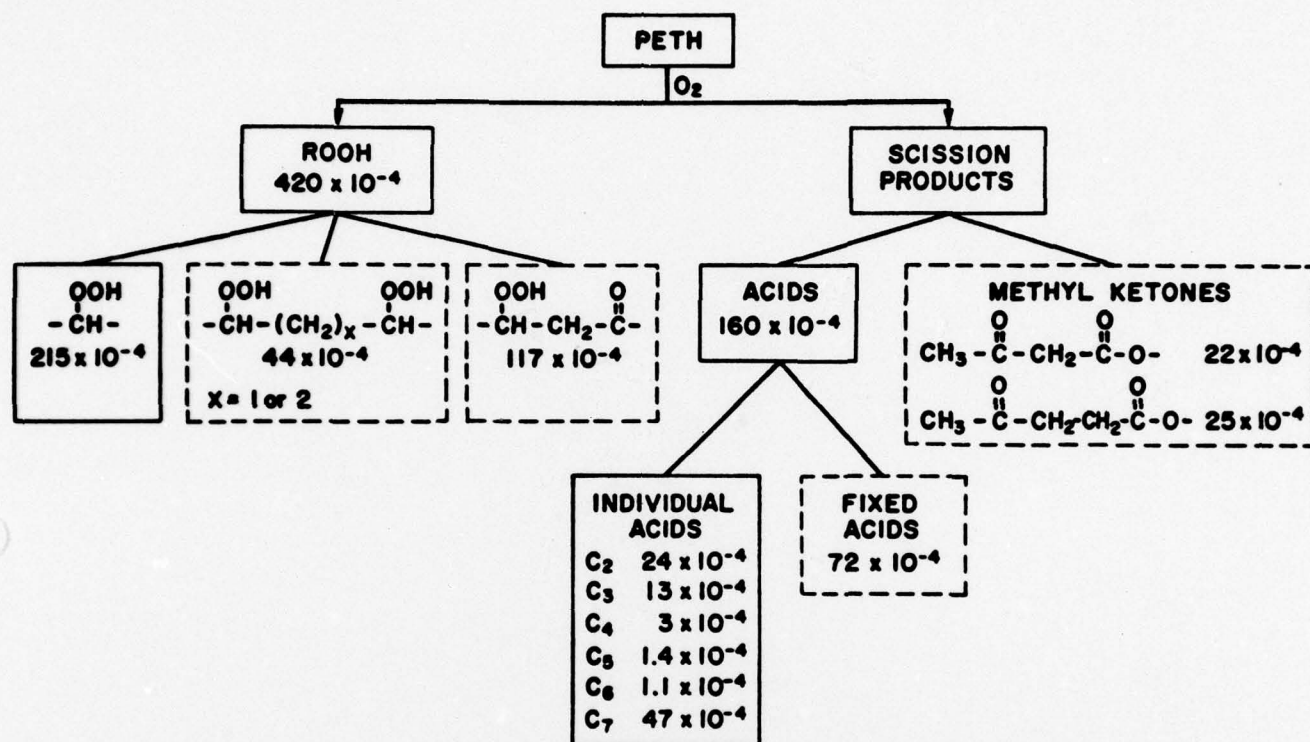


Fig. 7 - Estimates of concentrations (in M) of various oxidation products from PETH.

TABLE VI

Results of 4-Ball Wear Experiments with PETH

<u>Sample</u>	<u>Run Time (min)</u>	<u>Average Scar Diameter (mm)</u>	<u>$10^3 \times$ Wear Volume (mm^3)</u>	<u>$10^3 \times$ Wear Rate (mm^3/min)</u>
<u>A. Pure PETH</u>				
	5	0.42	0.90	
	15	0.49	2.0	
	30	0.53	3.0	0.06
	60	0.60	5.3	
	60	0.59	4.9	
<u>B. Oxidized PETH</u>				
($420 \times 10^{-4}\text{M}$	15	0.56	3.8	
Hydroperoxide)	30	0.71	10.9	0.48
	60	0.87	25.5	
<u>C. Mixtures of Pure and Autoxidized PETH</u>				
25 vol %	15	0.55	3.5	
Oxidized PETH	30	0.60	5.4	0.16
($105 \times 10^{-4}\text{M}$	60	0.70	10.2	
Hydroperoxide)				
50 vol %	15	0.57	4.2	
Oxidized PETH	30	0.67	8.5	0.28
($210 \times 10^{-4}\text{M}$	60	0.79	17.1	
Hydroperoxide)				

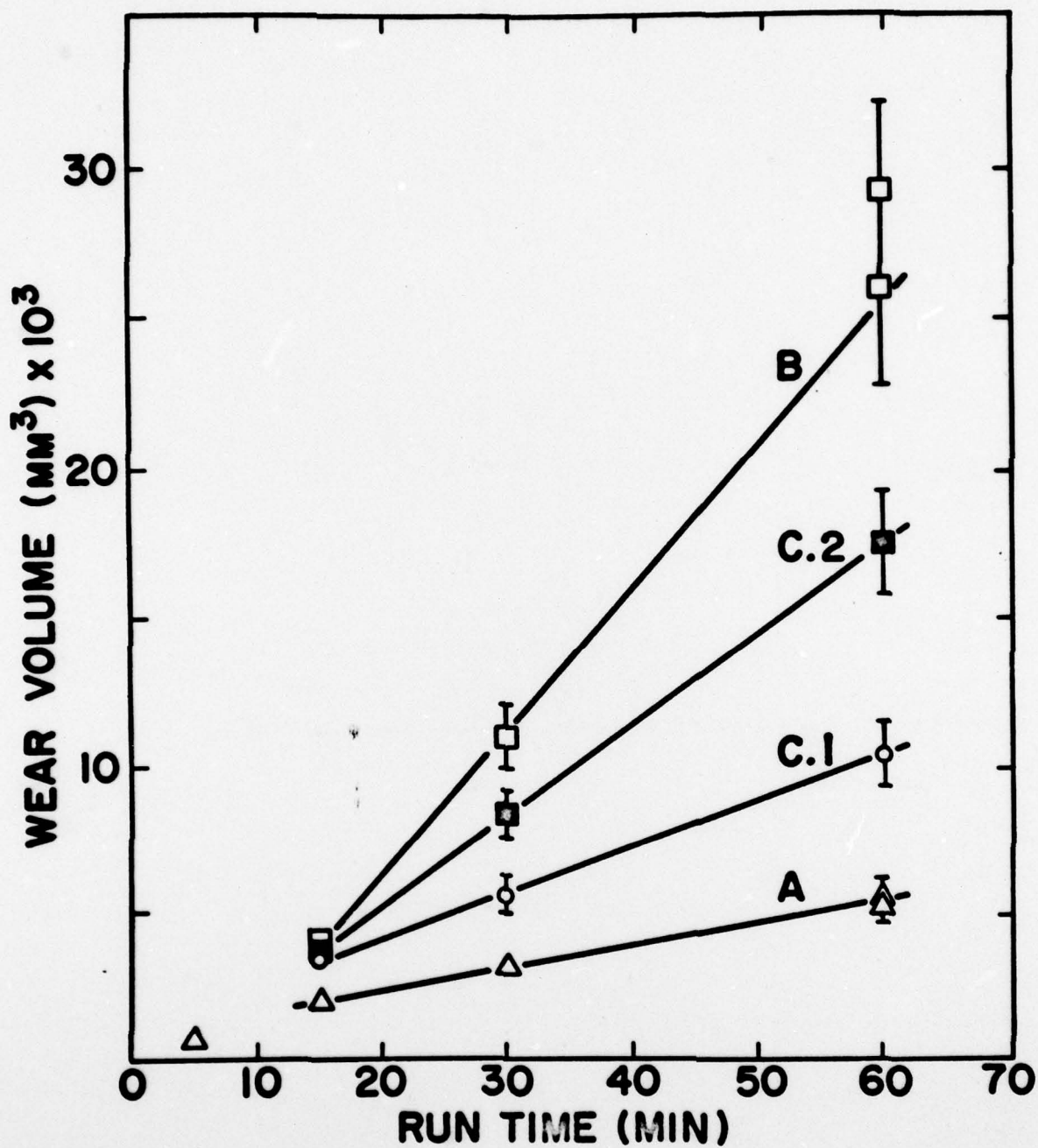


Fig. 8 - Wear volume vs. run time for pure (curve A) and oxidized PETH. Initial concentrations of hydroperoxides: A - 0, B - $420 \times 10^{-4}M$, C.1 - $105 \times 10^{-4}M$, C.2 - $210 \times 10^{-4}M$.

In order to assess the relationship between the increased wear rates noted in experiments with autoxidized PETH and the concentrations of oxidized components present in the PETH a series of wear experiments with admixtures of autoxidized and pure PETH were carried out. From the results of those experiments, cf. Table VIC and Figure 8, we conclude that the increased wear rates are directly proportional to the concentration of oxidized components present in PETH.

Soluble Iron Analyses - Analyses for soluble iron in all wear samples from oxidized PETH experiments reveal that the amounts of soluble iron closely corresponds to the total amounts of iron calculated by Feng's equation, assuming that the wear of the upper ball is equivalent to the total wear of the lower three balls in the wear apparatus. For these samples the ratio of soluble iron to that calculated is 1.05 with a standard deviation of 0.14.

For pure PETH and PETH with added acetic acid the ratios of soluble iron to calculated total iron increase with the time of the wear experiment as shown in Table VII.

Consumption of Hydroperoxide Species - The consumption of hydroperoxide species in wear experiments with oxidized and admixture of pure and oxidized PETH was followed by titration. The results of these analyses are shown in Table VIII. The rates of consumption are approximately proportional to the initial hydroperoxide concentration. The molar quantities of hydroperoxide consumed were much greater than the molar concentrations of soluble iron produced in the wear experiment.

TABLE VII

Soluble Iron in Wear Samples

<u>Sample</u>	<u>Run Time (min)</u>	<u>10^5 x Total Soluble Fe (g)</u>	<u>10^5 x Calculated Wear Fe (g)</u>	<u>Soluble Fe Wear Fe</u>
Pure PETH	15	1.04	3.18	.33
	30	2.32	4.79	.48
	60	8.4	8.16	1.04
Pure PETH + 9.5 x 10^{-4} M Acetic Acid	30	2.87	5.47	.52
	60	5.91	8.32	.71
Pure PETH + 86.7 x 10^{-4} M Acetic Acid	30	3.84	7.16	.54
Pure PETH + 462 x 10^{-4} M P_3	30	4.08	9.39	.43
Pure PETH + 462 x 10^{-4} M P_3O	30	6.23	8.47	.74

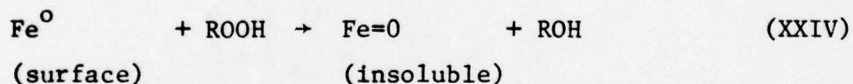
TABLE VIII

Consumption of Hydroperoxides

Run Time (min)	10^4 x Initial Hydroperoxide (M)	10^4 x Hydroperoxide Consumed (M)	10^4 x Soluble Iron (g atoms/l)
15	420	79	1.25
30		115	3.4
45		116	
60		195	
120		303.5	
15	210	-	1.25
30		6.2	-
60		11.4	6.6
15	105	-	1.25
30		38	2.5
60		61.5	4.1

Effects of Triphenylphosphine Reductions - Triphenylphosphine is a very selective reducing agent for hydroperoxide species which quantitatively reduces such species to the corresponding alcohols. The reduction of oxidized PETH with small amounts of triphenylphosphine have a dramatic effect on its wear behavior. From the results summarized in Table IX we see that upon the addition of an amount of triphenylphosphine sufficient to reduce ca. 10 percent of the total hydroperoxides a dramatic decrease in wear occurs. In ancillary experiments it was shown that the amount of hydroperoxide remaining after reduction corresponded closely to that calculated assuming a quantitative reaction of triphenylphosphine with hydroperoxide species.

Preliminary Model - Although it is premature to propose a detailed mechanochemical mechanism for the observed increased wear with autoxidized PETH, the results obtained thus far suggest that hydroperoxides species may play an important role in the wear process. One can envision sequences such as the following,



followed by a solubilization of the surface iron oxide species by β -dicarbonyl chelating species present in the oxidized PETH, i.e.,

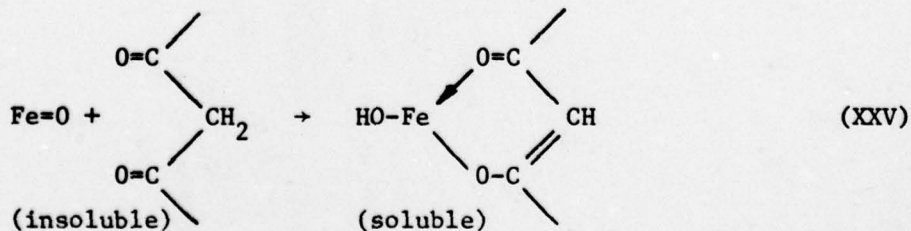


TABLE IX

Results of 4-Ball Wear Experiments
With Oxidized PETH ^a Reduced With Triphenylphosphine

Ratio ($\frac{\phi_3 P}{-OOH}$)	Run Time (min)	Average Scar Diameter (mm)	$10^3 \times$ Wear Volume (mm ³)
1.02	15	0.47	1.7
	30	0.53	3.1
	58	0.66	7.7
0.50	30	0.51	2.5
	60	0.51	2.5
0.10	30	0.45	1.33
0.04	30	0.741	13.1
	60	0.737	12.8
-	15	0.56	3.8
	30	0.71	10.9
	60	0.87	25.5

$$\text{^a } (-OOH) = 420 \times 10^{-4} M$$

To investigate the plausibility of such processes we now plan to carry out a study of the separate and the combined effects on wear of added pure hydroperoxide and dicarbonyl chelating species with pure PETH and with a model synthetic hydrocarbon lubricant.

EXPERIMENTAL

Materials - Pentaerythrityl tetraheptanoate, PETH, was purified by methods previously described to yield a PDP material.⁽¹³⁾

4,4'-methylenebis(2,6-di-tert-butylphenol), BPH, obtained from Aldrich Chemical Company was recrystallized twice from ethanol: mp 155°C. The sample of 2,6,3',5'-tetra-tert-butyl-4-hydroxyphenyl-4-methylene-2,5-cyclohexadiene-1-one, the quinone methide, QM, was prepared by the method of Coppinger.⁽¹⁵⁾

Batch Reactor; Design and Procedure - The batch reactor design resembles that of the stirred flow reactor⁽¹⁶⁾ in that it consists of two eccentric Pyrex glass spheres. The purified PETH (35 or 40 ml) was introduced under the flow of argon into the larger outside sphere (55 mm i.d.) and mixed using argon flow during the heating period followed by oxygen during the oxidation period. Both of these gases were introduced into the reactor through perforations (7 holes, 0.5 mm diameter) in a smaller inside sphere (20 mm o.d.) at a flow rate of 13.8 ml. sec⁻¹ at 180°. The batch reactor was used with the same gas supply system and constant temperature bath as those utilized for the stirred flow reactor.⁽¹⁶⁾ Solid samples of the antioxidant, 4,4'-methylenebis(2,6-di-tert-butylphenol), were introduced into the reactor before oxygen flow or after varying degrees of oxidation by means of a small glass ladle. The sample of antioxidant completely dissolved within a few seconds. Samples were then withdrawn from the reacting mixture at various time intervals, were quenched to room temperature, and were analyzed for hydroperoxide, (-OOH), by titration and for the remaining antioxidant utilizing liquid chromatographic methods.

Liquid Chromatographic Analysis - A Waters' HPLC system was used for analysis. The system consists of two Model 6000 solvent delivery pumps, a model U6K Septumless injector, a model 660 gradient programmer and a model 440 dual micro UV-VIS detector. A model FS-970 LC Spectrofluorometer from Schoeffel was connected downstream of the UV detector for fluorescence measurements.

HPLC analysis was accomplished by reverse-phase separation on a μ -Bondapak C_{18} column obtained from Waters. The column was operated at room temperature, and a 10 minute linear gradient of the mobile phase from 60/40 CH_3CN/H_2O to 100% CH_3CN was used for all the analyses reported here. The chromatographic peaks corresponding to bisphenol and quinone methide were identified by: a) retention time, b) coinjection of the standard and the mixture, and c) the ratios of their UV-Vis absorption response (peak areas) at 280 nm and 405 nm. The fluorescence response of BPH provides yet another means of identification and peak purity check.

Quantification was achieved using peak heights or peak areas compared with standard calibration mixtures. A Hewlett Packard Model 3380A integrator was used for all the peak area integrations.

Wear Experiments - The wear experiments were carried out utilizing a Roxanna modification of the Shell 4-ball friction and wear apparatus under dry air, with a bulk lubricant temperature equal to $100^{\circ}C$, under a load of 40 kg and at 600 rpm. This load is below the initial seizure load of ca. 50 kg determined in ancillary experiments.

Determination of Soluble Iron in Wear Samples - A 0.5 ml sample of PETH from the wear experiment was added to 0.5 ml of a 1.0 M solution of hydroquinone in ethanol. The resulting solution was then mixed with 4 ml of $1.5 \times 10^{-2}M$ solution of orthophenanthroline in ethanol. Upon mixing, a colored complex having an

absorption maximum at 5100 Å was formed. After 40 minutes the spectrum was recorded employing as a reference solution a mixture containing pure PETH in place of the PETH from the wear solution. Upon standing, a slow increase in absorbance after color development was observed in used PETH samples. This is perhaps due to slow oxidation of particulate iron. Utilizing solutions of ferric octanoate in pure PETH it was found that the absorbance at 5100 Å obeyed Beer's Law with a molar extinction coefficient based on Fe^{+3} equal to $1.15 \times 10^4 \text{ cm/M}$ to a concentration of at least $6 \times 10^{-5} \text{ M}$ in Fe^{+3} .

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